

Astron. Astrophys. Suppl. Ser. **64**, 453-467 (1986)

Time dependent chemistry in dense molecular clouds.

III. Infrared band cross sections of molecules in the solid state at 10 K

L. B. d'Hendecourt^(1,2) and L. J. Allamandola^(1,3)⁽¹⁾ Laboratory Astrophysics, Huygens Laboratorium, Wassenaarseweg 78, 2300 RA Leiden, The Netherlands⁽²⁾ Groupe de Physique des Solides de l'E.N.S., T23, 4 Place Jussieu, 75251 Paris, Cedex 05, France⁽³⁾ NRC Senior Associate, NASA Ames Research Center, Mail Stop 245/6, Moffett Field, CA. 94035, U.S.A.

Received June 20, accepted August 9, 1985

Summary. — Thin film transmission infrared spectra and a list of integrated absorbance values (band strengths) of bands in the 2.5 to 20 micron range of various molecular solids deposited on a CsI window cooled to 10 K are presented. These solids include molecules known or suspected to be present on interstellar grains such as H₂O, CO, NH₃ and CH₄ and mixtures of these molecules as well as various hydrocarbons. The method is described by which the absorbance values derived can be used to estimate column densities of species adsorbed on interstellar grains and other solids associated with celestial IR sources.

Key words : infrared radiations — interstellar medium : molecules.

1. Introduction.

Infrared spectroscopy is the most direct way to study the properties of dust in dense interstellar clouds. Numerous spectral features have been observed either in extinction or in emission in various sources (see Willner, 1984 for a review of the properties of the sources and Allamandola, 1984 for a review of the observed spectral features and their implications for the dust composition). Water ice, widely observed at 3250 cm⁻¹ (3.08 μm) in absorption towards dense (Aitken, 1981) and even less dense molecular clouds Whittet *et al.*, 1983), has been extensively studied in the laboratory. These studies have shown that, in the interstellar medium, water is present in the amorphous rather than crystalline ice form (Leger *et al.*, 1979). Hagen *et al.* (1981, 1983a) have carried out extensive measurements of the 3.1 μm ice band in many mixed molecular ices and derived optical constants which have been used to model the observed interstellar bands (Van de Bult and Greenberg, 1984). Observations as well as theoretical models taking gas and grain surface chemistry into account (Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985) show that although water is a dominant mantle constituent under most dense cloud conditions, it is not the only one. Ammonia, carbon monoxide and assorted hydrocarbons are present as well. Carbon dioxide, formaldehyde and methane are expected; O₂ and N₂ are also likely mantle constituents, but are infrared inactive. For the observations, the compact infrared source W33A shows one of the richest spectra in the 2.5 to 20 micron region (Soifer *et al.*, 1979). Besides the strong absorption band due to water ice, absorptions in the 5 to 8 micron region are observed which could be attributed to water, methanol and (or) other aliphatic hydrocarbons (Hagen *et al.*, 1980; Tielens *et al.*, 1984; d'Hendecourt, 1984). More recently, in the

same source, Lacy *et al.* (1984) observed two strong absorptions at 2143 cm⁻¹ (4.67 μm) and 2167 cm⁻¹ (4.62 μm); the first is due to solid CO, the second, although not completely characterized is strongly suggestive of C≡N. Quite recently, two other features have been detected at about 2050 and 2540 cm⁻¹ (Geballe *et al.*, 1985).

Although many bands arising from the ice component of interstellar dust have now been measured, comparatively little quantitative laboratory data is available with which one can extract column density information in spite of extensive studies performed in various matrices and mixtures of ices. These studies have been largely undertaken to qualitatively understand the changes likely to occur in the infrared spectra of ices as a result of various intermolecular interactions in the mixture (e.g. shifts and broadening of the lines). Infrared optical properties of thin cryofilms of a few molecules have been reported, see for example Wood and Roux (1982) and Fink and Sill (1982) and references therein as well as Hallam (1973) for a discussion of solid state effects. Hagen *et al.* (1983a, b) have carried out an extensive study of infrared spectra of binary mixtures with water but except for the 3 μm region, they do not report optical properties.

In order to extract more quantitative information from interstellar spectra we have measured the 2.5-20 micron absorption spectra of thin layers of some pure substances and mixtures which are representative of interstellar ices. The materials studied are listed in table I. These spectra, along with band assignments and integrated absorbance values, are presented in figure 1. These data can be used to calculate the column density of solid state molecules or functional groups absorbing in a particular region of the spectrum along a given line of sight and give an indication of the range over which these values can vary. Apart from

water, for which a value of the absorbance for the librational band (« 12 micron » ice band) is given, ammonia, methane, methanol and other hydrocarbons have been studied. Mixtures of some of these simple molecules with water (including carbon dioxide and acetonitrile) are displayed here. The hydrocarbons have been studied in order to evaluate the integrated absorbances for the vibrations of the aliphatic groups ($-\text{CH}_2$ and $-\text{CH}_3$) in the 3 and 7 micron regions. These are particularly important for the interpretation of the 3 micron observations of the galactic center and the 7 micron region in protostellar objects for which integrated intensities measured under realistic astrophysical conditions are lacking in the literature. An extensive discussion of the 2.5-20 μm spectrum of H_2O can be found in Hagen *et al.* (1983b) and references therein.

2. Experimental procedure.

Since the experimental details have been published elsewhere (Hagen *et al.*, 1979; Hagen *et al.*, 1981), only the salient points are discussed here. A closed cycle helium refrigerator (Air Products Displex) mounted in a vacuum chamber maintained at 2×10^{-7} mbar, cools the sample substrate, a CsI window, down to 10 K. The gaseous samples, pure substances or mixtures, are prepared in glass bulbs on a greaseless vacuum glass line. For our studies, the purity of the samples is not a crucial parameter since we are interested only by the strongest and most characteristic bands. Nonetheless, standard high purity gas handling techniques were used. Triply distilled water was further purified by three freeze-thaw cycles under vacuum. Methane (anhydrous, 99.96 %), ammonia (purity, 99.6 %), and carbon monoxide (99.997 %) were supplied by Matheson and used without further purification. Hydrocarbons and other substances were obtained from Baker (purity $\sim 99\%$) and generally purified before use, by several freeze-thaw cycles under vacuum. After preparation in the glass bulb, the gases are introduced into the sample vacuum chamber through a capillary tube directed perpendicularly to the cold window. The deposition rate and film thickness are measured by a laser interference technique. This deposition rate can be varied with a needle valve and is slow ($\sim 10 \mu\text{m h}^{-1}$ or 5×10^{-5} mole h^{-1}). In a few experiments, the thickness was measured at three different spots on the window within the IR beam area ($\sim 1 \text{ cm}^2$) showing that the sample thickness is constant to within 1 fringe over this range ($\lambda = 632.8 \text{ nm}$). Thin samples ($\lesssim 1$ micron) are used extensively to avoid interference effects in the infrared as well as saturation in the strongest bands. Infrared spectra were measured at 2 cm^{-1} resolution using a Fourier Transform Infrared Spectrometer (Digilab 15 B/D). In all cases, transmission spectra have been measured of freshly deposited samples at 10 K. Virtually all of the solids are amorphous since no thermal cycling took place.

3. Infrared spectroscopy.

3.1 INTEGRATED INTENSITY : DEFINITION AND UNITS. — To facilitate comparison between these data and those published in the literature, either chemical or astronomical, we briefly define the units used in our calculations. Detailed discussions can be found in Gribov and Smirnov (1962),

Wexler (1967), Pugh and Rao (1976) and Person (1981). Results on absolute infrared band intensities are given in these papers with units and conversion tables between the different units clearly presented.

The integrated intensity of an infrared absorption band is related to the electron charge displacement which occurs in a chemical bond during a vibration. A change in the dipole moment vector with vibrational coordinate is required for an infrared photon to be absorbed. The absolute intensity is then given by (Wexler, 1967) :

$$I = \left(\frac{v_i}{\omega} \right) \frac{N\pi}{3c^2} \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \quad (1)$$

where N is the number of molecules per unit volume, c the speed of light, $\left(\frac{\partial \mu}{\partial Q_i} \right)$ the rate of change of the dipole moment vector, μ , with respect to the i th normal coordinate Q_i , ω the frequency of the transition and v_i the absorption frequency.

Following Person (1981), the intensity A of a vibrational band is defined as the integrated absorbance

$$A = \frac{1}{Cl} \int_{v_1}^{v_2} \ln(I_0/I) dv \quad (2)$$

where C is the concentration of the absorbers, often expressed as moles per liter (or molecules per cm^3), l is the pathlength of the infrared beam through the material, v the frequency in cm^{-1} , I_0/I is the ratio of the incident to the transmitted beam, with the integration performed over the band. Note that natural logarithms are used here. Although the observed band shape is a convolution product of the true band shape with the response function of the spectrometer (resolution), a basic rule of thumb for correct band shape measurements using conventional dispersion instruments is that the true full width at half maximum (FWHM), Δv , should be

$$\Delta v_i > 5S \quad (3)$$

where S is the spectral slit width (Russell and Thompson, 1957; Person, 1981). Ramsay (1972) notes that when $\Delta v_i \approx S$, the case which holds for many interstellar ice band measurements using circular variable filter wheels and cooled grating spectrometers, the error in the integrated absorbances should be no worse than 20-50 %, with the larger error holding for irregularly shaped bands. The uncertainty of 20 %, typical for most of the bands measured here, is acceptable in view of the other uncertainties which accumulate in such experiments such as the precise number of absorbers in the beam and baselines which are sometimes difficult to establish. This latter problem is also one which is often severe in astronomical spectra. In our experiments, all the spectra have been measured with a resolution of 2 cm^{-1} so that most of the bands satisfy the condition given by equation (3) and no bands of FWHM smaller than 5 cm^{-1} have been taken into account.

The A values listed in figure 1 captions have been obtained by measuring I , with the laser interference technique and using a standard peak area program provided by Digilab Inc. to evaluate the integral. The largest uncertainty arises

from evaluating C , the concentration of absorbers, as the densities of these solids are not accurately known. We have assumed the densities to be constant (1 g/cm^3) and the samples uniformly thick across the 1.13 cm^2 area probed by the IR beam. These assumptions, combined with l and the molecular weight, give the concentration. The units of A can be expressed in many ways : for example from equation (2), it could be in $\text{liters mole}^{-1} \text{ cm}^{-2}$ if C is in moles per liter, or in cm molecule^{-1} if C is expressed in molecules per cm^3 , this last unit, more convenient, is used throughout our results.

For a near Lorentzian shaped band, the integral over the absorption band can be approximated by

$$\int_{\nu_1}^{\nu_2} \ln(I_0/I) d\nu \simeq \tau_{\max} \Delta\nu_{1/2} \quad (4)$$

for symmetrically shaped bands where τ_{\max} is $\ln(I_0/I)$ at the maximum of the band (the optical depth) and $\Delta\nu_{1/2}$ is the full width of the band at half maximum (FWHM). Given the values for A , one can calculate the column density ($N = Cl$) of absorbers responsible for a given

absorption band by substituting equation (4) into equation (2) and rearranging to

$$N \simeq \frac{\tau \cdot \Delta\nu}{A} \quad (5)$$

This has been applied to the 6.0 and $6.8 \mu\text{m}$ bands in some protostars by Tielens *et al.* (1984) and d'Hendecourt *et al.* (1986) to determine the column density of H_2O and carbon in aliphatic groups on grains towards these sources. Similarly, Lacy *et al.* (1984) have used this technique to determine the amount of solid CO and CN towards several protostars. Their calculation of the solid CO column density, based on the 2140 cm^{-1} band towards NGC7538 (IRS9), is reviewed here as illustrative of the method. Lacy *et al.* measured

$$\int \ln(I_0/I) d\nu \left(\equiv \int \tau \nu d\nu \right) = 11.1 \text{ cm}^{-1},$$

$$\tau_{\max} = 2.09 \quad \text{and} \quad \Delta\nu = 5.0 \text{ cm}^{-1}.$$

Using $A = 1.06 \times 10^{-17} \text{ cm molecule}^{-1}$ for solid CO (Jiang *et al.*, 1975), and substituting into equation (5), the amount of CO in the 2140 cm^{-1} band is calculated.

$$N = \frac{11.1 \text{ cm}^{-1}}{1.06 \times 10^{-17} \text{ cm molecule}^{-1}} \simeq \frac{(2.09)(5.0 \text{ cm}^{-1})}{1.06 \times 10^{-17} \text{ cm molecule}^{-1}} \simeq 1 \times 10^{18} \text{ molecules cm}^{-2}.$$

Adding the contribution from the 2135 cm^{-1} CO band yields $N(\text{CO}_{\text{solid}}) = 1.8 \times 10^{18} \text{ molecules cm}^{-2}$, the value they list in their table III. The interstellar CN A value has recently been narrowed down on the basis of laboratory experiments, and the CN column density has been revised (d'Hendecourt *et al.*, 1986).

3.2 INFRARED SPECTRA. — The compounds and mixtures studied are listed in table I. Infrared spectra are displayed between 4000 and 500 cm^{-1} (2.5 to 20 microns) in figure 1a to r. Every spectrum displayed has been taken with 2 cm^{-1} resolution. Absorbance values are indicated on each spectrum in units of $\log_{10}(I_0/I)$. The name, formula and thickness (l) of the substance appear directly on the figure. Below each spectrum, a table caption is given which contains the assignments of the main bands and references, the precise frequency of maximum absorption, the full width of the band at half maximum, $\Delta\nu(\text{FWHM})$, in wavenumbers, the optical depth ($\tau_{\max} = \ln(I_0/I)$) at the given peak absorption and the integrated intensity expressed in cm molecule^{-1} , calculated from equations (2) or (4). Comments are given for each spectrum, including references to the astrophysical implications.

4. Discussion and conclusion.

It is not the purpose of this paper to extensively discuss either the properties of each molecule regarding its infrared spectrum or the possible interactions between different molecules in mixtures. Some discussion of these questions

has already been given by Hagen *et al.* (1983b) where many useful references can be found. This paper complements that work by providing integrated intensities.

Comparison of the data listed in figure 1 with previously published data shows that the integrated intensities for some of the various molecular bands do not differ by much from the gas phase intensities (see, for example, Gribov and Smirnov, 1962; Pugh and Rao, 1971 and Person, 1981); for example the integrated intensity of the methane deformation mode does not change in the solid compared to the gas phase although the band is somewhat broadened in mixtures. Similar behaviour has been reported for carbon monoxide, not measured here, but carefully studied by Jiang *et al.* (1975) and discussed by Person (1981). Water, of course is the well known exception for which the OH stretching mode has an intensity in the solid state 25 times greater than in the gas phase value (Hagen *et al.*, 1981). The highly polar CO_2 molecule shows similar but opposite behaviour : when diluted in argon (0.1%) or in water (10%), the intensity of the antisymmetric C=O vibration at 2340 cm^{-1} ($4.27 \mu\text{m}$) has a value comparable to that in the gas phase. In pure solid CO_2 however a reduction in intensity ($\div 4$ to 5) is observed due to intermolecular interactions between two neighbouring molecules.

This type of behaviour is qualitatively described in Hagen *et al.* (1983b) and Person (1981). For water, we find that the intensity of the librational mode is, on the average, 8 times less intense than the OH stretching mode. As already described by Hagen and Tielens (1982), this libra-

tional mode is observed at 13.3 micron for amorphous water, is symmetric and very broad ($\Delta\nu = 250 \text{ cm}^{-1}$). This band, as well as the less symmetric 6 micron bending mode, is not very sensitive to the environment of the water molecule, and does not disappear in mixtures. Consequently it should be observed in space, since confusion by substantial overlap with the 10 micron silicate feature is not likely. However, because of its broad and shallow nature, it might be quite difficult to recognize in actual astronomical spectra. Carbon dioxide is, unfortunately, not observable from the ground at 4.27 or 15.1 micron due to its abundance at high altitudes in the Earth's atmosphere. However, its very strong absorbance at 4.27 micron (2350 cm^{-1}), 10 times that of CO, should make it one of the first candidates to look for when observations from space will become possible. The 10 times weaker 15.1 micron CO₂ band, which has not been studied here, should be searched for in the IRAS spectra although the low resolution of the instrument should make a confident detection difficult.

Unfortunately, all of the strongest fundamentals of NH₃ overlap the water lines so that any quantification of NH₃ in these regions is meaningless if the exact ratio of the two molecules is not known in advance. Complexes of water with ammonia give rise to a long wavelength wing on the ice band. This wing has been studied by Hagen *et al.* (1983a). The umbrella mode of NH₃, near 10 micron, is specific for solid ammonia but, unfortunately, is not obvious in astronomical spectra due to blending with the silicate band. The constancy of this band in pure ammonia as well as in mixtures with water, makes it an extremely useful probe of the amount of ammonia present.

For the hydrocarbons, alcohols and the acetate, the absorbance values deduced from the spectra presented in figure 1 for the various lines (CH stretching and deformation modes in CH₃ and CH₂ groups) show large variations from one molecule to another. It is important to realize that, except for the simplest molecules, complete deconvolution of the CH stretching and deformation bands in terms of CH₂ and CH₃ groups is impossible. Thus, the *A* values given for each individual group include overlap among the various components. Given the generally low resolving power of most astronomical spectrometers, it is probably best to sum up *A* values in each region and treat them collectively. A further complication arises since in species such as CH₄, CH₃OH and CH₃CN, the 3.4 and 6.8 μm bands are due to one aliphatic group, whereas in molecules such as pentane, cyclohexane and octanol, each molecule contains several aliphatic groups. We have assumed that the density of the ices is constant

in order to estimate the number of molecules within each sample. Thus, while the total *A* value for the CH stretching modes, per molecule, in pentane (C₅H₁₂), hexane (C₆H₁₄) and octanol (C₈H₁₈O) are nearly 10 times greater than in CH₄, each individual CH bond contributes an amount comparable to that in CH₄. A similar analogy is impossible for the various deformation modes since, in this case, the intensity is much more sensitive to the neighbouring groups. Nonetheless, in view of the need for a mean with which to estimate column densities, an average of the *A* values for the CH stretching and deformation modes in saturated hydrocarbons is useful.

Unfortunately, both the absolute and relative integrated absorbance values for the CH stretching and bending modes depend on the nature of the group they are adjacent to in the molecule, making an unambiguous column density determination difficult at best. When adjacent to unsaturated groups, the *A* values for stretching vibrations tend to decrease, while for the deformation modes they tend to increase. Thus, for ethylacetate, $A(\text{str}) \cong 5 \times 10^{-18}$ and $A(\text{def}) \cong 10^{-17}$ while for pentane $A(\text{str}) \cong 6 \times 10^{-17}$ and $A(\text{def}) \cong 6 \times 10^{-18}$. The values for methanol fall within these extremes with $A(\text{str}) \cong 3 \times 10^{-17}$ and $A(\text{def}) < 10^{-17}$. All these values are in units of cm molecule^{-1} . Of course, if the molecule containing some unsaturated groups has several aliphatic groups adjacent to one another, they will act more like saturated hydrocarbons such as pentane and hexane. Until spectra are available which cover both the 3.4 and 6-8 μm regions, only limits can be placed on the column densities of saturated hydrocarbons. These questions are considered in Tielens *et al.* (1984), d'Hendecourt (1984) and d'Hendecourt *et al.* (1986).

Finally, the spectra of mixtures 1 and 2 show that the band intensities do not seem to vary by more than a factor of two, even in fairly complex mixtures. The spectra, and integrated absorbance values are discussed in detail in d'Hendecourt *et al.* (1986).

Acknowledgements.

We wish to sincerely thank Drs. L. van Dijk for the considerable experimental work he carried out in measuring infrared reflection spectra of some of these ices. We thank Dr. A. G. G. M. Tielens for numerous discussions and a critical reading of the manuscript.

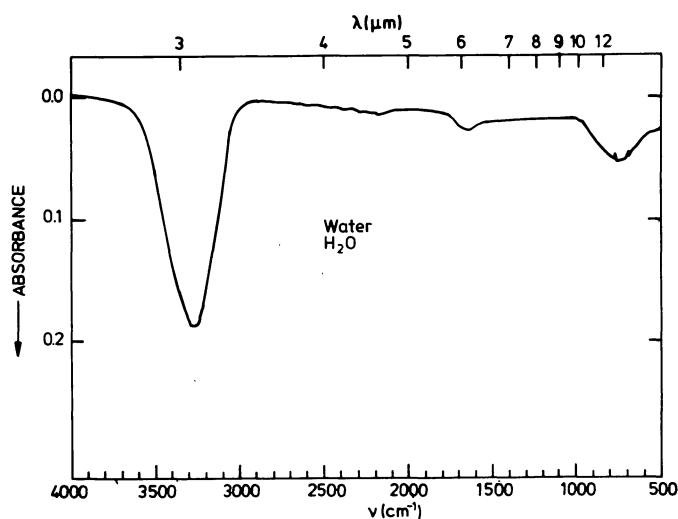
References

- AITKEN, D. K. : 1981, in « Infrared Astronomy », *IAU Symp.*, No. 96, eds. Wynn-Williams, C. G. and Cruickshank, D.P. (D. Reidel Publishing Co., Dordrecht) p. 207.
- ALLAMANDOLA, L. J. : 1984, in *Galactic and Extragalactic Infrared Spectroscopy*, eds. M. F. Kessler and J. P. Phillips (D. Reidel Publishing Co., Dordrecht) p. 5.
- BELLAMY, L. J. : 1956, in *The Infrared Spectra of Complex Molecules* (London, Methuen and Co. Ltd.; New York, John Wiley and Sons, Inc.)
- BERTIE, J. E., MORRISON, M. M. : 1980, *J. Chem. Phys.* **73**, 4832.
- FALK, M., WHALLEY, E. : 1961, *J. Chem. Phys.* **34**, 1554.
- FINK, V., SILL, G. T. : 1982, in *Comets*, L. L. Wilkening ed. (University of Arizona Press) p. 164.
- FRANCIS, S. A. : 1951, *J. Chem. Phys.* **19**, 942.
- GEBALLE, T., BAAS, F., GREENBERG, J. M., SCHUTTE, W. : 1985, *Astron. Astrophys.* **146**, L6.

- GRIBOV, L. A., SMIRNOV, V. N. : 1962, *Sov. Phys., Usp.* **4**, 919.
- GRIM, R. J. A., D'HENDECOURT, L. B. : 1986, submitted to *Astron. Astrophys.* (paper IV).
- HAGEN, W., ALLAMANDOLA, L. J., GREENBERG, J. M. : 1979, *Astrophys. Space Sci.* **65**, 215.
- HAGEN, W., ALLAMANDOLA, L. J., GREENBERG, J. M. : 1980, *Astron. Astrophys.* **86**, L3.
- HAGEN, W., TIELENS, A. G. G. M. and GREENBERG, J. M. : 1981, *Chem. Phys.* **56**, 367.
- HAGEN, W. and TIELENS, A. G. G. M. 1982, *Spectrochim. Acta* **38A**, 1089.
- HAGEN, W., TIELENS, A. G. G. M., GREENBERG, J. M. : 1983a, *Astron. Astrophys.* **117**, 132.
- HAGEN, W., TIELENS, A. G. G. M., GREENBERG, J. M. : 1983b, *Astron. Astrophys. Suppl. Series* **51**, 389.
- HALLAM, H. E. : 1973, in *Vibrational Spectroscopy of Trapped Species*, H. E. Hallam, ed. (Wiley, London) p. 67.
- D'HENDECOURT, L. B. : 1984, Ph. D. Thesis, University of Leiden, The Netherlands.
- D'HENDECOURT, L. B., ALLAMANDOLA, L. J., GREENBERG, J. M. : 1985, *Astron. Astrophys.* **152**, 130 (paper I).
- D'HENDECOURT, L. B., ALLAMANDOLA, L. J., GRIM, R. J. A., GREENBERG, J. M. : 1986, *Astron. Astrophys.* in press (paper II).
- HERZBERG, G. : 1945, in *Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules*, van Nostrand (ed.) (Princeton, New Jersey).
- JIANG, G. J., PERSO, W. B. and BROWN, K. G. : 1975, *J. Chem. Phys.* **62**, 1201.
- KITTA, K. and KRATSCHMER, W. : 1983, *Astron. Astrophys.* **122**, 105.
- LACY, J. H., BAAS, F., ALLAMANDOLA, L. J., PERSON, S. F., MCGREGOR, P. J., LONSDALE, C. J., GEBALLE, T. R., VAN DE BULT, C. E. P. : 1984, *Astrophys. J.* **276**, 533.
- LEGER, A., KLEIN, J., DE CHEVEIGNE, S., GUINET, C., DEFOURNEAU, D., BELIN, M. : 1979, *Astron. Astrophys.* **79**, 256.
- PERSON, W. B. : 1981, in *Matrix Isolation Spectroscopy*, A. J. Barnes et al. (eds.), (D. Reidel Publishing Company) p. 415.
- POUCHERT, C. J. : 1983, in *The Aldrich Library of Infrared Spectra* (Aldrich Chemical Company, Milwaukee, Wisconsin).
- PUGH, L. A., RAO, K. N. : 1976, in *Molecular Spectroscopy : Modern Research*, Vol. II, K. N. Rao, ed. (Academic Press, New York) p. 165.
- RAMSAY, D. A. : 1952, *J. Am. Chem. Soc.* **74**, 72.
- RUSSELL, R. A., THOMPSON, H. W. : 1957, *Spectrochim. Acta* **9**, 133.
- SCHIMANOUCI, T. : 1972, in *Tables of Molecular Frequencies Consolidated Vol. 1*, NSDRS-NBS no. 39.
- SOCRATES, G. : 1981, in *Infrared Characteristic Group Frequencies* (John Wiley and Sons ed., New York).
- SOIFER, B. T., PUETTER, R. C., RUSSELL, R. W., WILLNER, S. P., HARVEY, P. M. and GILLET, F. C. : 1979, *Astrophys. J.* **232**, L53.
- TIELENS, A. G. G. M., HAGEN, W. : 1982, *Astron. Astrophys.* **114**, 245.
- TIELENS, A. G. G. M., ALLAMANDOLA, L. J., BREGMAN, J., GOEBEL, J., D'HENDECOURT, L. B., WITTEBORN, F. C. : 1984, *Astrophys. J.* **287**, 697.
- VAN DE BULT, C. E. P. M. and GREENBERG, J. M., 1984, *Mon. Not. R. Astron. Soc.* **210**, 803.
- WEXLER, A. S. : 1967, *Applied Spectroscopy Reviews* **1**, 29.
- WHITTET, D. C. B., BODE, M. F., LONGMORE, A. J., BAINES, D. W. T., EVANS, A. : 1983, *Nature* **303**, 218.
- WILLNER, S. P. : 1984, in *Galactic and Extragalactic Infrared Spectroscopy*, eds. M. F. Kessler and J. P. Phillips (D. Reidel Publishing Co., Dordrecht) p. 22.
- WOOD, B. E., ROUX, J. A. : 1982, *J. Opt. Soc. Am.* **72**, 720.

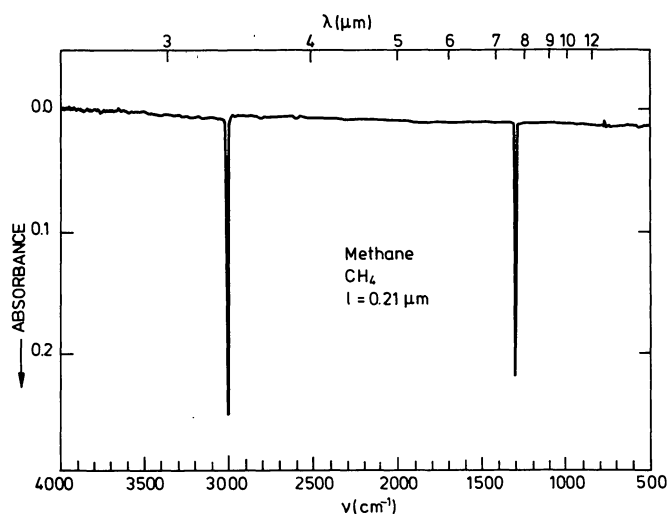
TABLE I. — *List of molecules and mixtures for which infrared spectra are displayed in figures 1a to r.*

H ₂ O (water)	C ₈ H ₁₇ O (octanol)
CH ₄ (methane)	C ₄ H ₈ O ₂ (ethylacetate)
NH ₃ (ammonia)	C ₂ H ₃ ON (methylisocyanate)
CH ₃ OH (methanol)	H ₂ O:NH ₃ (3:1)
CH ₃ CN (methylcyanide)	H ₂ O:CH ₃ OH (3:1)
n-C ₅ H ₁₂ (n-pentane)	H ₂ O:CH ₃ CN (5:1)
n-C ₆ H ₁₄ (n-hexane)	H ₂ O:CO ₂ (9:1)
Cyclo-C ₆ H ₁₂ (cyclohexane)	H ₂ O:CO:CH ₄ :NH ₃ (6:2:1:1)
C ₇ H ₁₄ (methylcyclohexane)	H ₂ O:O ₂ :CO:CH ₄ :NH ₃ :N ₂ (1:1:1:0.3:0.3:0.03)



Vibration	Frequency (cm ⁻¹)	Δν(FWHM)	Absorbance	A(cm.molecule ⁻¹)
OH-stretch	3275	335	1.70 × 10 ⁻¹	2.0 × 10 ⁻¹⁶
OH-bend	1670	160	1.50 × 10 ⁻²	8.4 × 10 ⁻¹⁸
H ₂ O libration	750	240	3.10 × 10 ⁻²	2.6 × 10 ⁻¹⁷

Comments. — The thickness has not been measured in this case. Integrated intensity for OH stretch is taken from Hagen *et al.* (1981). The corresponding thickness is 0.23 micron. Note that the so-called « 12 micron band » characteristic of crystalline water ice, peaks at 13.3 micron for water in the amorphous ice form, is extremely broad (11.4 to 16 microns at halfwidth) and has an integrated intensity 7.7 times weaker than the OH stretching vibration. For a thorough description of the behaviour of this last band upon warm up see Hagen and Tielens (1982) and Kitta and Kratschmer (1983). See Hagen *et al.* (1983a, b) and references therein for a very thorough study of the spectrum of water in various solids. The 6 micron band profile is somewhat distorted from that of pure amorphous ice because of absorption by gas phase H₂O present in the purge of the spectrometer.

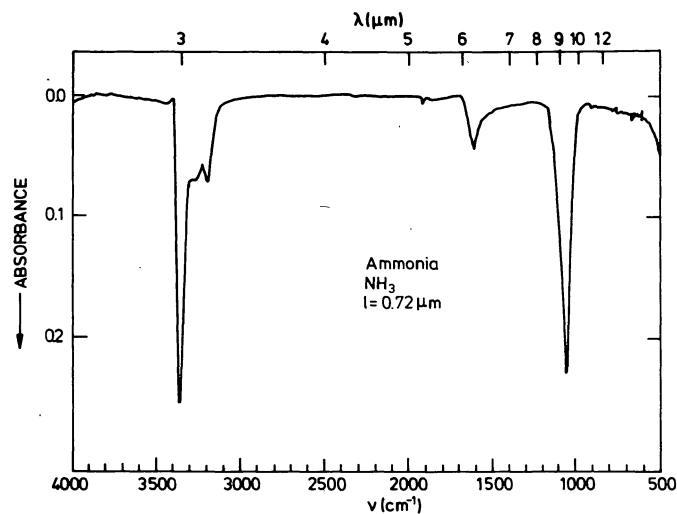


Vibration	Frequency (cm ⁻¹)	Δν(FWHM)	Absorbance	A(cm.molecule ⁻¹)
CH-stretch	3010	7	2.5×10^{-1}	6.4×10^{-18}
CH-deformation	1302 1297	8	2.1×10^{-1}	6.1×10^{-18}

Comments. — The CH deformation mode appears as a doublet in pure methane. The integrated intensities of the deformation modes are equal to the values given by Gribov and Smirnov (1962) for gas phase CH₄ of 5.7×10^{-18} . The stretching mode *A* value is half its gas phase value of 1.2×10^{-17} .

References

Schimanouchi (1972).

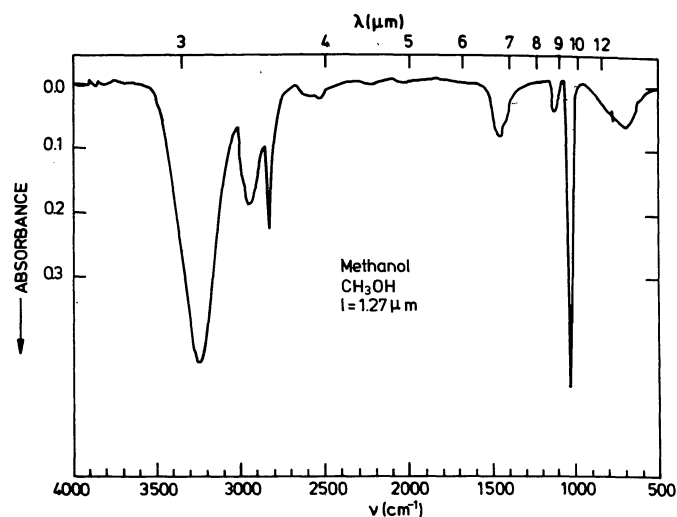


Vibration	Frequency (cm ⁻¹)	Δν(FWHM)	Absorbance	A(cm.molecule ⁻¹)
NH-stretch	3375	45	2.5×10^{-1}	1.1×10^{-17}
NH-deformation	1624	-	4.4×10^{-2}	-
"umbrella" mode	1070	68	2.2×10^{-1}	1.7×10^{-17}

Comments. — The absorbance and Δν of the NH stretch are determined for the 3375 cm⁻¹ component to calculate the integrated intensity. When integrated over the whole band (3420-3120 cm⁻¹), $A = 2.2 \times 10^{-17}$. *A* for the NH deformation mode has not been calculated; the extremely asymmetric character of the band, due to the very long, long-wavelength wing, makes it difficult to define the baseline. The umbrella mode is strongly perturbed in the solid phase and is very intense. In an interstellar spectrum this band will not be prominent due to the obscuration by the 10 micron silicate feature. However, this band is of great value in evaluating the amount of ammonia in laboratory simulated grain mantles (d'Hendecourt *et al.*, 1986).

References

Bertie and Morrison (1980).

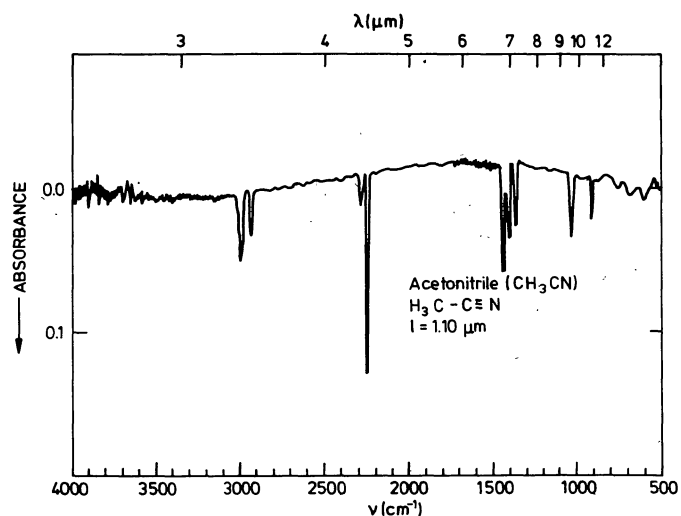


Vibration	Frequency (cm ⁻¹)	$\Delta\nu$ (FWHM)	Absorbance	$A(\text{cm.molecule}^{-1})$
OH-stretch	3250	235	4.3×10^{-1}	1.1×10^{-16}
CH-stretch	2982	100	1.7×10^{-1}	2.1×10^{-17}
CH-stretch	2950			
CH-stretch	2828	30	2.1×10^{-1}	7.6×10^{-18}
CH ₃ -deformation	1477	90	8.3×10^{-2}	1.0×10^{-17}
CH ₃ -deformation	1455			
OH-bend	1415			
CH ₃ -rock	1124	34	4.7×10^{-2}	1.3×10^{-18}
CO-stretch	1026	29	4.7×10^{-1}	1.8×10^{-17}
torsion	700	200	6.6×10^{-2}	1.6×10^{-17}

Comments. — Although the integration over the entire 1450 band ($1600\text{--}1300\text{ cm}^{-1}$) has no strict physical meaning, the possibility to fit the interstellar 1470 cm^{-1} band of protostellar objects with a mixture of water and methanol (Tielens *et al.*, 1984) justifies such an evaluation. If this identification is confirmed, this data is extremely important in placing limits on the column density of methanol along the line of sight. The torsion mode is analogous to the librational mode of water.

References

Falk and Whalley (1961).
Hagen *et al.* (1983b).

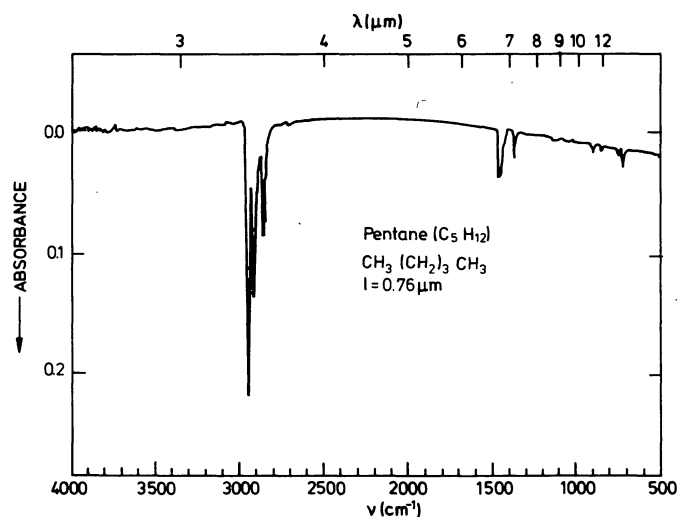


Vibration	Frequency (cm ⁻¹)	$\Delta\nu$ (FWHM)	Absorbance	$A(\text{cm.molecule}^{-1})$
CH-stretch	3001	19	4.9×10^{-2}	1.5×10^{-18}
CH-stretch	2941	11	3.3×10^{-2}	4.7×10^{-19}
CN-stretch	2286	16	2.1×10^{-2}	2.3×10^{-18}
CN-stretch	2252			
CH ₃ -deformation	1447	17	7.4×10^{-2}	2.2×10^{-18}
?	1409	15	5.2×10^{-2}	1.4×10^{-18}
CH ₃ -deformation	1373	17	4.4×10^{-2}	1.0×10^{-18}
CH ₃ -rock	1038	22	4.6×10^{-2}	1.3×10^{-18}
CC-stretch	917	7	2.9×10^{-2}	2.0×10^{-19}

Comments. — The CH modes appear at 3001 and 2941 (symmetric and antisymmetric) and are weak. The main C≡N absorption occurs at 2252; the importance of this band is described at length in d'Hendecourt *et al.* (1986). The apparent structure from 4000 to about 3200 cm^{-1} and from 800 to 500 cm^{-1} as well as the sinusoidal behaviour of the baseline running throughout the spectrum are artifacts produced by microphonics improperly filtered out of the transformation.

References

Herzberg (1945).
Schimanouchi (1972).

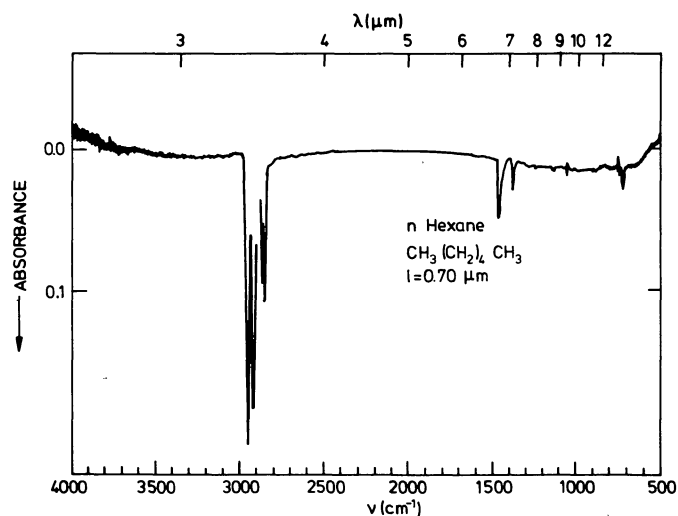


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm \cdot molecule^{-1})$
CH-stretch CH_3	2957	17	2.0×10^{-1}	2.3×10^{-17}
CH-stretch CH_2	2923	20	1.6×10^{-1}	2.4×10^{-17}
CH-stretch CH_3	2872	9	6.2×10^{-2}	4.8×10^{-18}
CH-stretch CH_2	2857	14	8.4×10^{-2}	9.0×10^{-18}
CH_2 -scissoring	1470	25	4.2×10^{-2}	6.0×10^{-18}
CH_2 -bending	1457		3.1×10^{-2}	
CH_3 -deformation	1372	11	2.2×10^{-2}	1.0×10^{-18}
	727	7	1.6×10^{-2}	7.3×10^{-19}

Comments. — The weaker, low frequency modes which arise from torsion and bending motions within the carbon chain are less useful as diagnostics and not treated quantitatively.

References

Bellamy (1956).
Pouchert (1983).

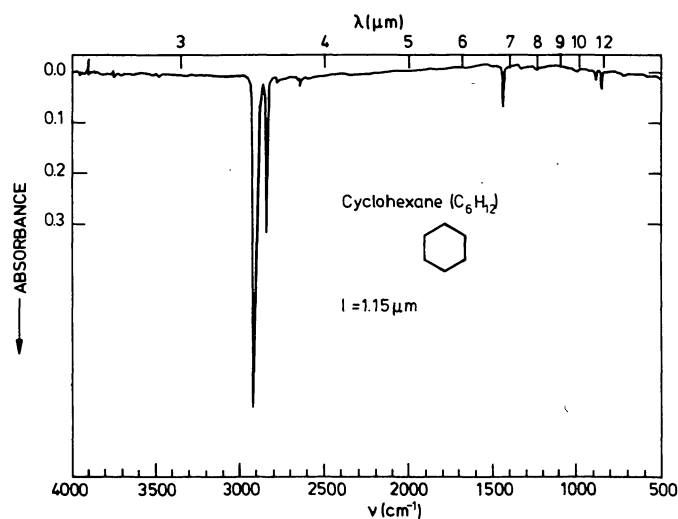


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm \cdot molecule^{-1})$
CH-stretch CH_3	2955	18	2.2×10^{-1}	2.2×10^{-17}
CH-stretch CH_2	2921	28	1.4×10^{-1}	2.2×10^{-17}
CH-stretch CH_3	2870	10	6.4×10^{-2}	3.6×10^{-18}
CH-stretch CH_2	2858	10	6.5×10^{-2}	3.6×10^{-18}
CH_2 -scissoring	1470	9	3.7×10^{-2}	1.9×10^{-18}
CH_3 -deformation	1460	40	3.4×10^{-2}	7.6×10^{-18}
CH_3 -deformation	1370	10	2.5×10^{-2}	1.4×10^{-18}
	910	-	-	-
	865	-	-	-
	765	-	-	-
	730	10	1.6×10^{-2}	9.0×10^{-19}

Comments. — The weaker, low frequency modes which arise from torsion and bending motions within the carbon chain are less useful as diagnostics and not treated quantitatively.

References

Bellamy (1956).
Pouchert (1983).

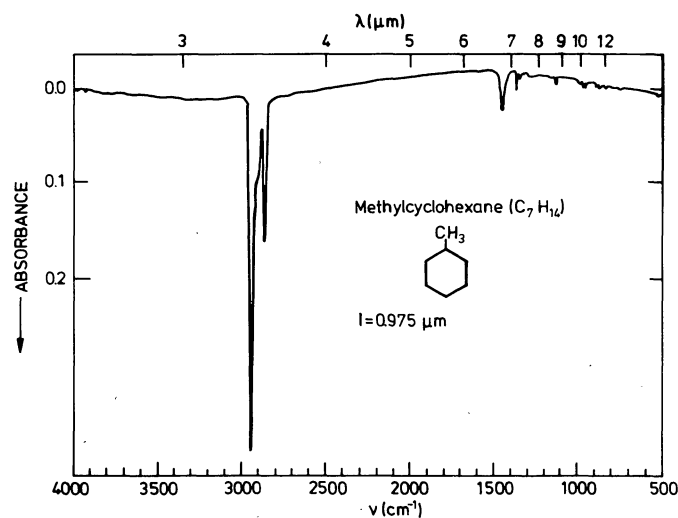


Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm} \cdot \text{molecule}^{-1})$
CH-stretch	2927	17	6.3×10^{-1}	5.3×10^{-17}
CH-stretch	2850	11	3.1×10^{-1}	1.4×10^{-17}
CH ₂ -scissoring	1452	13	8.4×10^{-2}	4.2×10^{-18}
CH ₂ -rock	903	8	2.0×10^{-2}	4.8×10^{-19}
CC-stretch	862	6	3.8×10^{-2}	8.0×10^{-19}

Comments. — Saturated hydrocarbon containing only CH₂ groups. The weaker bands between 1400 and 1000 cm⁻¹ are due to CH₂ wagging, twisting and rocking motions.

References

Bellamy (1956).
Pouchert (1983).

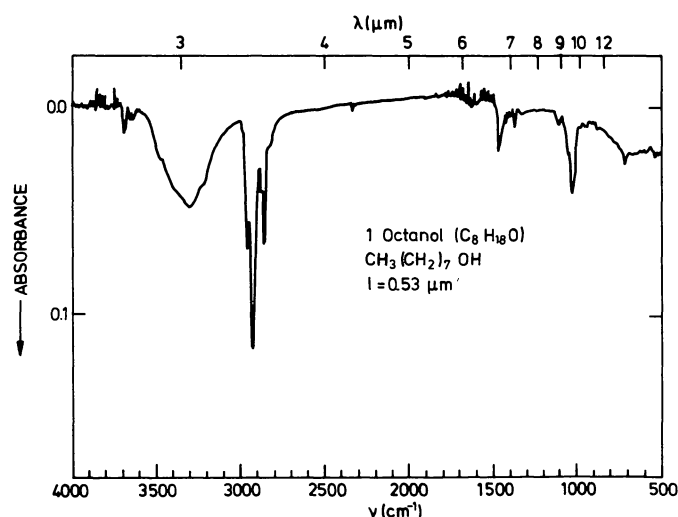


Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm} \cdot \text{molecule}^{-1})$
CH-stretch CH ₃	2946	20	3.8×10^{-1}	3.3×10^{-17}
CH-stretch CH ₂	2926	-	-	-
CH-stretch CH ₂	2908	-	-	-
CH-stretch CH ₃	2868	16	1.6×10^{-1}	1.1×10^{-17}
CH-stretch CH ₂	2850	-	-	-
CH-deformation	1475	50	1.4×10^{-2}	3.0×10^{-18}
CH-deformation CH ₃	1462			
CH-deformation CH ₂	1452			
CH-deformation CH ₃	1373	9	7.2×10^{-3}	2.8×10^{-19}
	1139	5	1.1×10^{-2}	2.4×10^{-19}
	1007	9	5.3×10^{-3}	2.0×10^{-19}
	981	6	1.1×10^{-2}	2.8×10^{-19}

Comments. — The weaker bands shortward of 1373 cm⁻¹ are due to various wagging, twisting and rocking motions as well as CH₃-ring torsional modes.

References

Pouchert (1983).

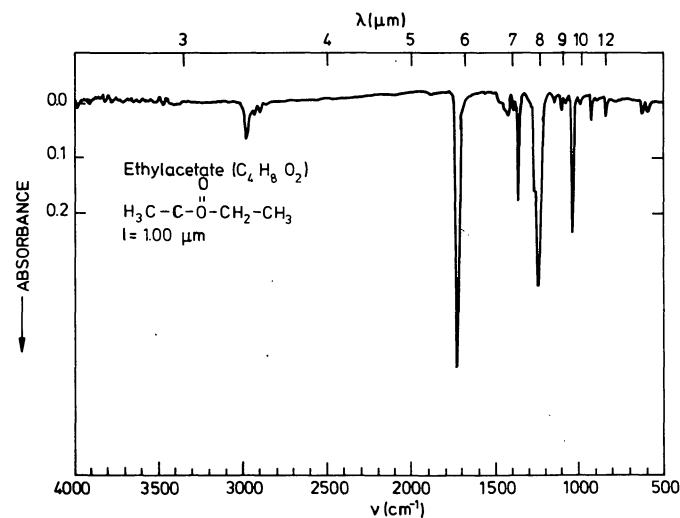


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm.molecule^{-1})$
OH-stretch	3310	270	2.3×10^{-2}	1.2×10^{-16}
CH-stretch CH_3	2961	26	2.5×10^{-2}	6.6×10^{-18}
CH-stretch CH_2	2932	26	9.5×10^{-2}	2.5×10^{-17}
CH-stretch CH_3	2876	10	1.1×10^{-2}	1.1×10^{-18}
CH-stretch CH_2	2860	16	4.3×10^{-2}	6.9×10^{-18}
CH-deformation CH_2	1465	—	3.0×10^{-3}	—
CH-deformation CH_3	1381	8	7.7×10^{-3}	6.2×10^{-19}
CO-stretch	1045	30	3.3×10^{-2}	1.0×10^{-17}

Comments. — The OH-stretch in this alcohol has the same value as that in methanol. This molecule has 75 fundamental vibrations, many of which overlap. This table lists only the unambiguous modes. In such a large molecule, the uncertainty associated with determining the precise number of molecules in the sample is reflected in a larger uncertainty in the A value. See section 4 for a further treatment of this point.

References

Socrates (1981).
 Pouchert (1983).

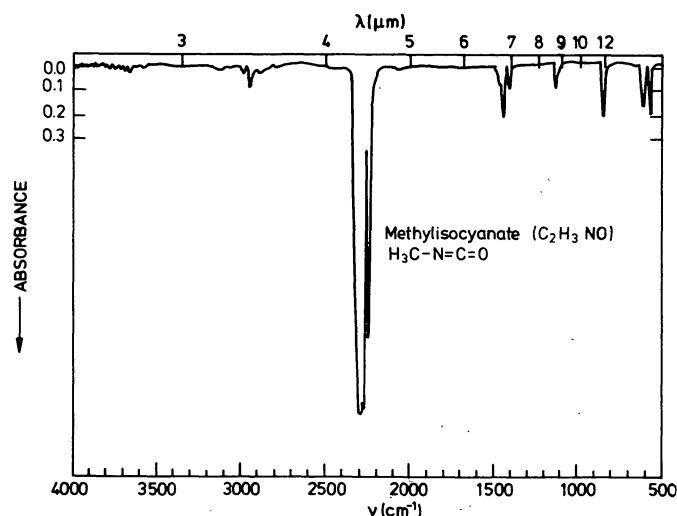


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm.molecule^{-1})$
CH-stretch CH_3	2986	21	5.9×10^{-2}	4.5×10^{-18}
CH-stretch	2940	17	1.4×10^{-2}	3.1×10^{-19}
CH-stretch	2907	20	2.0×10^{-2}	1.8×10^{-19}
CO-stretch	1738	20	5.1×10^{-1}	3.9×10^{-17}
CH_2 -deformation	1450	—	3.6×10^{-2}	7.7×10^{-18}
CH_3 -deformation	1375	10	2.0×10^{-1}	0.8×10^{-17}
CO-stretch	1255	60	3.7×10^{-1}	5.0×10^{-17}
CO-stretch	1050	50	2.6×10^{-1}	1.6×10^{-17}
OC_2H_5 -bend	855	10	3.6×10^{-2}	1.3×10^{-18}

Comments. — This molecule is included to demonstrate the strong variations possible in the infrared cross sections of methyl and methylene groups ($-CH_3$ and $-CH_2-$), when an unsaturated group, in this case a carbonyl ($C=O$) is adjacent. For the CH_3 deformation mode at 1375, A is markedly increased ($\times 5$) whereas the CH stretch in the 2900 region is markedly decreased ($\div 10$) with respect to the values aliphatic groups have in saturated molecules such as pentane and hexane. Methanol represents an intermediate case. This effect is particularly important to interpret data pertaining to grain mantle composition where CO is present in abundance and where intermediates such as $CH_3-C=O$ can be produced as a result of UV photolysis of ice mixtures (d'Hendecourt *et al.*, 1986). Note the strong absorption due to the $C=O$ stretch at $1738 cm^{-1}$. This absorption ($1850 > \nu > 1600 cm^{-1}$) should be carefully searched for in interstellar spectra. If found, it would indicate the presence of carbonyl as well as the importance of UV photolysis of icy mantles on grains.

References

Francis (1951).
 Bellamy (1956).
 Pouchert (1983).

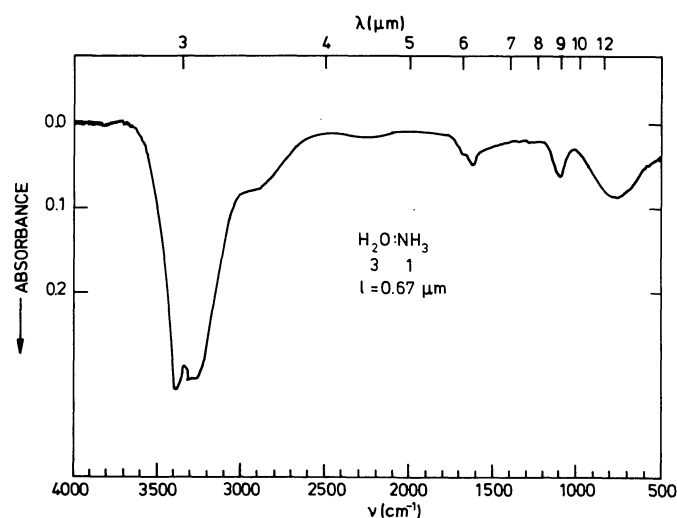


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm.molecule^{-1})$
CH-stretch	3000			
CH-stretch	2958			(7.5×10^{-18})
CH-stretch	2905			
CH-stretch	2805			
N=CO-stretch	2305			$> 10^{-16}$
CH-deformation	1460			
CH-deformation	1440			
CH-deformation	1412			
CO-stretch	1135			(2.8×10^{-18})

Comments. — The A values are very uncertain because the thickness of this sample has not been measured with the interference technique but roughly estimated from the deposition time and the flow rate. A thickness of about 1.4 micron has been estimated. The $-N=C=O$ stretch is completely saturated so that the absorbance value is a lower limit. This band is extremely strong and broad and it is to be noted that it does not appear in UV photolysis experiments (d'Hendecourt *et al.*, 1986) although its position, close to the CO_2 antisymmetric stretching vibration, should make it difficult to detect unequivocally. The lower limit of A for this band is 10^{-16} . Isothiocyanates, $N=C=S$, have a very strong band at 2050 cm^{-1} analogous to the $N=C=O$ band. This 2050 band is a candidate for matching a weak observed feature in W33A (Geballe *et al.*, 1985). Note the strong absorption band in the 1450 region and the relatively weak absorption at 2900 cm^{-1} , illustrating the effect that aliphatic groups adjacent to unsaturated groups undergo band strength reversal with respect to those adjacent to saturated groups. See the spectra of pentane, hexane and ethylacetate.

References

Bellamy (1956).
Pouchert (1983).

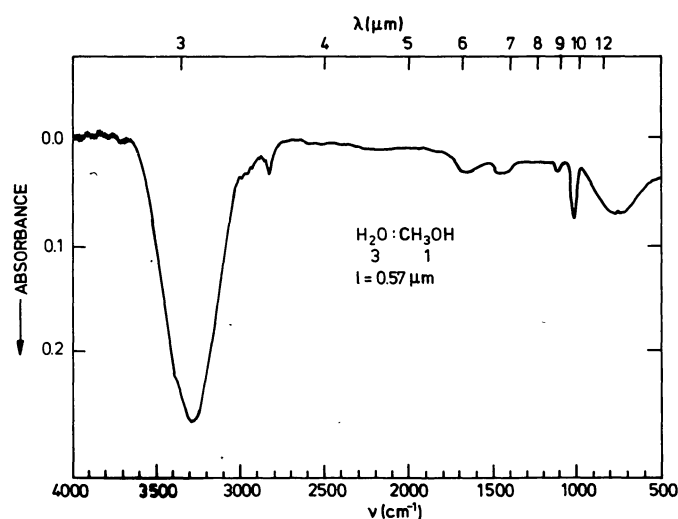


Vibration	Frequency (cm^{-1})	$\Delta\nu(FWHM)$	Absorbance	$A(cm.molecule^{-1})$
NH-stretch	3385	—	3.1×10^{-1}	
NH-deformation	1625	—	3.5×10^{-2}	
OH bend	1670	—		
Umbrella mode	1110	70	3.8×10^{-2}	1.2×10^{-17}

Comments. — The description of mixtures of ammonia and water is given to a full extent in Hagen *et al.* (1983b). The occurrence of NH and OH stretching and deformation modes, in the same region, together with complicated interactions (i.e. long wavelength wing on the 3 micron ice band), makes the evaluation of the integrated intensities of little use if one does not know precisely the $H_2O:NH_3$ ratio. The umbrella mode is remarkably insensitive to the environment in position, width and intensity and, as such, can be used to determine the amount of NH_3 present; for pure NH_3 , $A = 1.7 \times 10^{-17}$; here it is 1.2×10^{-17} . Features due to H_2O are not listed in the table.

References

Hagen *et al.* (1983a, b).

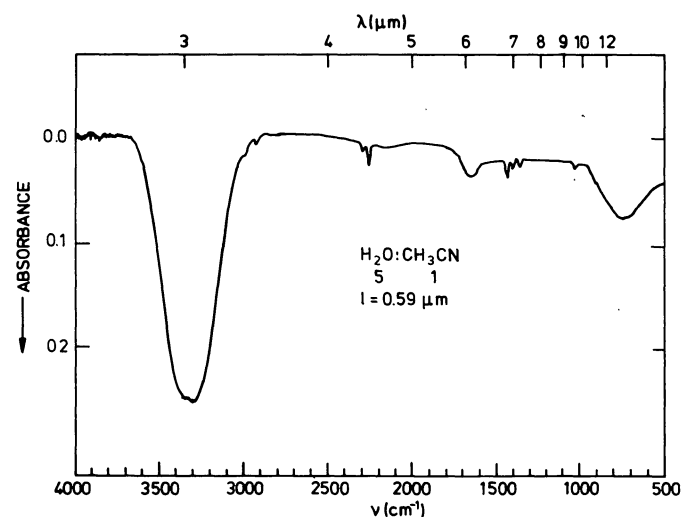


Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm.molecule}^{-1})$
CH-stretch	2993	-	-	-
CH-stretch	2938	-	-	-
CH-stretch	2830	20	2.4×10^{-2}	5.1×10^{-18}
CH ₃ -deformation	1478	85		4.5×10^{-18}
CH ₃ -deformation	1450			
OH-bend (CH ₃ OH)	1426			
CH ₃ -rock	1125	24	9.0×10^{-3}	1.3×10^{-18}
CO-stretch	1018	32	5.0×10^{-2}	1.0×10^{-17}

Comments. — Although the CH-stretching modes at 2993 and 2938 cm⁻¹ are strong in pure CH₃OH, mixing with water makes it impossible to calculate the integrated intensity of these lines. The other absorbance value seem to be reduced by a factor of 2. This is probably significant, as the CH₃ rocking mode keeps the same intensity. Features which overlap those due to H₂O as well as those arising from H₂O are not treated here.

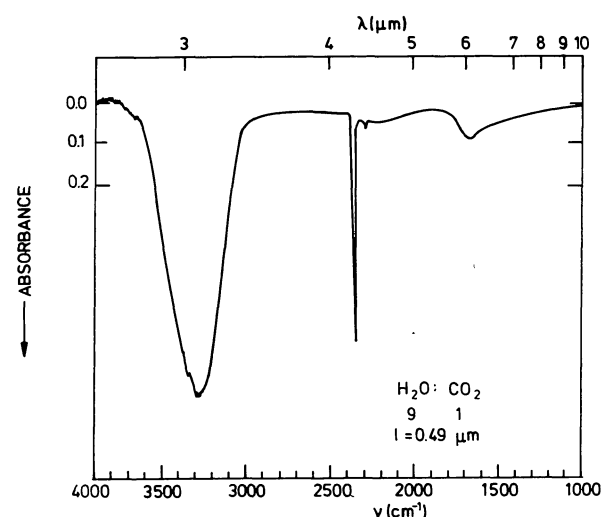
References

Hagen *et al.* (1983b).



Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm.molecule}^{-1})$
CH ₃ -stretch	3004	-	-	8.1×10^{-19}
CH ₃ -stretch	2942	13	6.4×10^{-3}	4.8×10^{-19}
CN-stretch	2296	12	8.3×10^{-3}	3.7×10^{-18}
CN-stretch	2264	14	2.0×10^{-2}	
CH ₃ -deformation	1445	14	7.3×10^{-3}	9.2×10^{-19}
	1410	15	9.6×10^{-3}	1.3×10^{-18}
CH ₃ -deformation	1372	13	1.6×10^{-2}	8.4×10^{-19}
CH ₃ -rocking	1039	12	7.7×10^{-3}	9.5×10^{-19}
CC-stretch	921	10	4.5×10^{-3}	3.7×10^{-19}

Comments. — The determination of the intensity of the 3004 cm⁻¹ band is rather uncertain due to the problem of baseline determination in the wing of the ice band. The position of the CN band is not shifted significantly in water. Although its strength increases slightly compared to that in solid CH₃CN, it is difficult to judge if this increase is significant or not since the other modes also show variations of this order. Features due to H₂O are listed in this table.

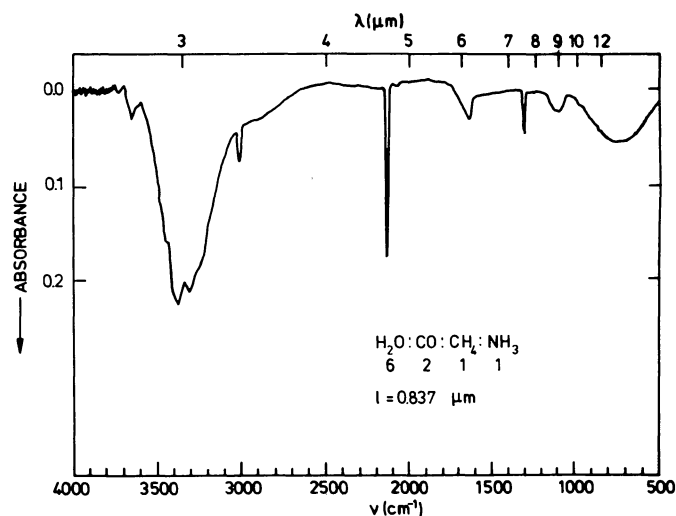


Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm.molecule}^{-1})$
Overtone (CO ₂)	3701	12	2.2×10^{-2}	2.0×10^{-18}
Overtone (CO ₂)	3645	19	2.5×10^{-2}	3.6×10^{-18}
CO-stretch	2340	18	5.3×10^{-1}	7.3×10^{-17}
O=C=O bend	656	(18)	-	(8.0×10^{-18})

Comments. — This spectrum has been recorded only from 3900 to 1000 cm⁻¹ (2.56 to 10 μm). The strength of the 2340 cm⁻¹ band is such that it should be easily observable (from space) as a constituent of grain mantles even if the abundance of CO₂ is only a to 10 % of that of solid CO, which has been observed in a few protostellar objects (Lacy *et al.*, 1984). The antisymmetric CO stretching vibration (Shimanouchi, 1972), absorbs so strongly that detection of the ¹³CO₂ isotope at 2280 cm⁻¹ should also be possible. The integrated intensity of the 2340 cm⁻¹ band of carbon dioxide mixed in water has a value comparable to that of 8.3×10^{17} , obtained from gas phase measurements (Gribov and Smirnov, 1962) and to the value obtained in highly diluted (1000/1) argon/CO₂ matrices (d'Hendecourt, 1984; Grim and d'Hendecourt, 1985). In solid CO₂, however, the intensity of this band is reduced by a factor of 4-5. This reduction in intensity is probably due to strong intermolecular forces only possible in pure frozen CO₂ although the exact reason for this decrease is not understood. The CO₂ bending mode (656 cm⁻¹) has not been measured here, but irradiation experiments where mixtures of ices (H₂O, CO, CH₄ and NH₃) have been photolyzed with ultraviolet light, producing substantial amounts of CO₂, show that the ratio of the intensities of the 2340 to the 656 cm⁻¹ lines leads to an integrated intensity of the order of 8×10^{-18} cm.molecule⁻¹, close to the gas phase value of 7.5×10^{-18} (Gribov and Smirnov, 1962). Although the spectral range is incomplete, this band is included here because it should be actively searched for in IRAS spectra although its strength combined with the low resolution of the IRAS spectrometer will make it difficult to detect.

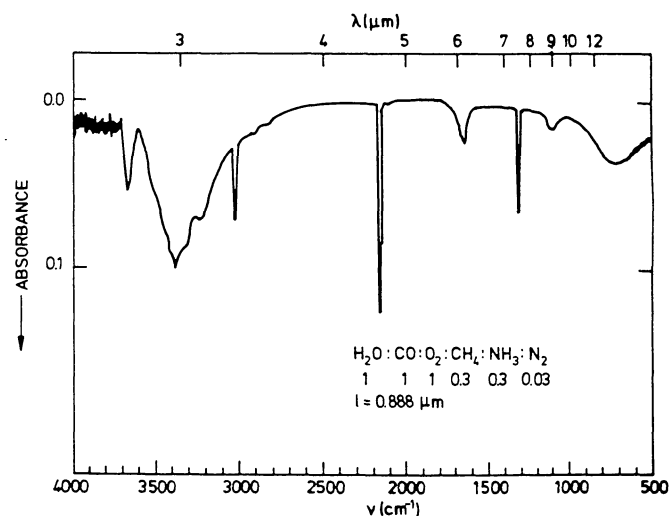
References

Schimanouchi (1972).



Vibration	Frequency (cm ⁻¹)	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm.molecule}^{-1})$
OH-stretch				
Free OH	3650	60	2.3×10^{-2}	-
OH-stretch				
CH-stretch CH ₄	3011	12	3.7×10^{-2}	-
CO-stretch	2138	11	1.8×10^{-1}	1.1×10^{-17}
H ₂ O/NH ₃ Bend	1640	-	-	-
CH ₄ -deformation	1304	12	4.7×10^{-2}	6.1×10^{-18}
"umbrella mode" NH ₃	1115	70	2.3×10^{-2}	1.4×10^{-17}
H ₂ O-libration	750	2	4.6×10^{-2}	2.2×10^{-17}

Comments. — This mixture corresponds to the water rich mixture described in d'Hendecourt *et al.* (1985b) and which has been used in ultraviolet photolysis studies in connection with the gas/grain model of interstellar molecule formation (d'Hendecourt *et al.*, 1985a). The purpose of including this calibrated spectrum is to demonstrate the extent to which the integrated intensities of the individual molecules change in complex mixtures. In general the change is not substantial, for example for CH₄ (3013 and 1305) and CO (2139), only the width of these bands is somewhat increased. CO has been widely studied in various solid environments and its absorption intensity at 2140 cm⁻¹ is quite similar in the gas phase and in various matrix materials (Jiang *et al.*, 1975). The intensity of NH₃ umbrella mode is also rather constant and constitutes a useful probe of UV photolysis efficiency in the experiments described in the above reference. Naturally, water and ammonia together have superimposed and sometimes complex vibrational band systems, which renders their estimation difficult. A description of these effects can be found in Hagen *et al.* (1983b). The derived A values do indeed vary to within a factor of 2, compared to the cross sections already given. These variations are however not significant in view of the uncertainties which arise during the preparation of complex mixture bulbs. Keeping the same cross sections as those derived in the preceding pages implies that the mixture ratio of H₂O, CO, CH₄ and NH₃ is 6, 2.7, 0.71 and 0.87.



Vibration	Frequency (cm^{-1})	$\Delta\nu(\text{FWHM})$	Absorbance	$A(\text{cm.molecule}^{-1})$
OH-stretch				
Free OH	3660	50	2.6×10^{-2}	-
OH-stretch "ice"				
CH-stretch CH_4	3013	14	4.4×10^{-2}	6.0×10^{-18}
CO-stretch	2139	9	1.2×10^{-1}	6.7×10^{-18}
$\text{H}_2\text{O}/\text{NH}_3$ Bend	1640	-	-	-
CH_4 -deformation	1305	9	6.2×10^{-1}	7.6×10^{-18}
Umbrella NH_3	1108	70	1.0×10^{-2}	6.0×10^{-18}
H_2O -libration	725	250	2.0×10^{-2}	1.9×10^{-17}

Comments. — These results are similar to those given on the preceding page for mixture 1. Note the strong free OH absorption at 3600 cm^{-1} due to water molecules not completely incorporated in an ice lattice (di, tri and higher polymers). The librational mode of water around 13 micron is slightly less intense (1.4) than in pure water. Methane is not affected. CO shows a change in intensity reflecting, presumably, an underabundance of it compared to the desired ratio. The actual composition of the mixture is probably closer to $\text{H}_2\text{O}/\text{CO}/\text{O}_2/\text{CH}_4/\text{NH}_3/\text{N}_2 = 1/0.76/X/0.6/0.23/Y$. $\text{O}_2(X)$ and $\text{N}_2(Y)$ are naturally not observed in the infrared.